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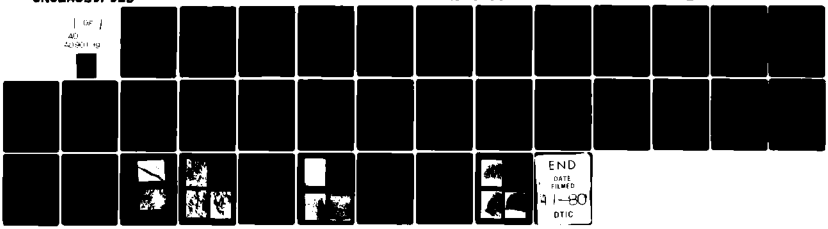

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The phenomena of slow strain-rate embrittlement was studied in three metal-interstitial systems, tantalum-oxygen, vanadium-oxygen and tantalum-nitrogen.

The embrittlement of tantalum by oxygen was investigated on specimens containing four levels of oxygen -- 0.33, 0.50, 0.85 and 1.30 atomic percent. All of the compositions showed embrittlement between 500-1000K in specimens deformed at $\dot{\epsilon} = 8.8 \times 10^{-4} sec^{-1}$. Associated with the embrittling phenomenon,

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Study of the vanadium-oxygen system also showed an embrittlement region between 600-875K. This embrittlement was accompanied by a yield stress plateau between 400-600K, an increasing work hardening rate between 300-650K and serrated yielding from 525K to 650K. A high level of titanium impurity limited testing to low oxygen concentrations.

Tests on the tantalum-nitrogen system concluded that nitrogen did not produce slow strain-rate embrittlement in this metal although it served as a potent room temperature strengthener. The interval in which embrittlement is expected in this metal is at a sufficiently high temperature that dynamic recovery and softening take place.

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SLOW STRAIN-RATE EMBRITTLEMENT IN TANTALUM DUE TO OXYGEN AND SELECTED EXPERIMENTS IN THE VANADIUM-OXYGEN AND TANTALUM-NITROGEN SYSTEMS

Abstract

The phenomena of slow strain-rate embrittlement was studied in three metal-interstitial systems, tantalum-oxygen, vanadium-oxygen and tantalum-nitrogen.

The embrittlement of tantalum by oxygen was investigated on specimens containing four levels of oxygen -- 0.33, 0.50, 0.85 and 1.30 atomic percent. All of the compositions showed embrittlement between 500-1000K in specimens deformed at $\dot{\varepsilon} = 8.8 \times 10^{-4} sec^{-1}$. Associated with the embrittling phenomenon, and occurring in the same temperature range where the ductility is dropping, are three dynamic strain-aging effects: (a) a yield stress plateau from 300-600K, (b) serrated yielding from 453-600K and an increasing work hardening rate from 300-600K. Scanning electron microscope studies show that failures were by microvoid coalescence at low temperatures changing to a predominantly intergranular mode in the embrittlement range.

Study of the vanadium-oxygen system also showed an embrittlement region between 600-875K. This embrittlement was accompanied by a yield stress plateau between 400-600K, an increasing work hardening rate between 300-650K and serrated yielding from 525K to 650K. A high level of titanium impurity limited testing to low oxygen concentrations.

Tests on the tantalum-nitrogen system concluded that nitrogen did not produce slow strain-rate embrittlement in this metal although it served as a potent room temperature strengthener. The interval in which

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embrittlement is expected in this metal is at a sufficiently high temperature that dynamic recovery and softening take place.

I. List of Publications

1. "Evidence for Slow Strain-Rate Embrittlement in Tantalum Due to Oxygen," Scripta Metallurgica, Vol. 13, pp. 491-496, A. E. Diaz and R. E. Reed-Hill.
2. "Comparison of Hydrogen and Oxygen Slow Strain-Rate Embrittlements," manuscript submitted for publication in the Proceedings of the Third International Conference on the Effects of Hydrogen on the Behavior of Metals, by R. E. Reed-Hill.

II. Participating Scientific Personnel

1. R. E. Reed-Hill, Principal Investigator
2. A. E. Diaz, Graduate Research Assistant

III. Degrees Awarded

1. Master of Science awarded to A. E. Diaz, August 1980.

IV. Statement of the Problem Studied and Scientific Importance

Although it was suggested some years ago that slow strain-rate embrittlement due to interstitial elements other than hydrogen should be possible, a clear cut verification of this hypothesis was missing until the recent discovery of the phenomena in niobium due to oxygen. The fact that niobium can be embrittled by oxygen in the temperature range from 500 to 900°K implies that careful consideration has to be given to

avoiding contamination of this metal by oxygen if it is to be used inside this temperature interval. The commercial significance of this conclusion should be obvious. However, oxygen is not the only interstitial element that could possibly cause slow strain-rate embrittlement. Nor is niobium the only transition metal in which interstitials may be able to cause such harmful effects. A basic understanding of the true extent to which slow strain-rate embrittlement presents a problem in the use of an important group of refractory metals such as the Type Va transition metals should be of considerable interest. Thus, in the research that was performed, a primary goal was to survey the extent to which the various Type Va metals are subject to slow strain-rate embrittlement. At the same time, the nature of the variation of the embrittlement phenomena with temperature, strain-rate and concentration of the interstitial element was determined.

Since the niobium-oxygen system has been investigated as a part of another project and the niobium-carbon system apparently offers the least promise of all the systems, only systems based on tantalum and vanadium were investigated. As the first step in the proposed research, the tantalum-oxygen and tantalum-nitrogen systems were investigated. These two systems should have been the most susceptible to significant slow strain-rate embrittlement. With these systems, it was possible to compare phenomena involving two different interstitials, oxygen and nitrogen. The third system investigated was the vanadium-oxygen system.

From the scientific point of view, this investigation of slow strain-rate embrittlement should lead to a better understanding of this embrittlement phenomena in general. Furthermore, it should make possible

the selection of a system (or systems) that holds the most promise for explaining the fracture mechanisms involved in slow strain-rate embrittlement. By examining such a system (or systems) in detail at a later time, it should also be possible to gain a better insight into the more difficult problem to investigate, that of the hydrogen embrittlement of steels.

V. Summary of Results

A. Procedure

The pure metals used in this study to prepare the alloys were supplied by Materials Research Corporation, Orangeburg, New York. The manufacturer's analyses for VP grade tantalum and vanadium are listed in Tables 1 and 2. The metal was supplied as 6.35 mm rod tantalum and 12.7 mm rod vanadium. In either case the stock rods were cold swaged to 3.2 mm without an intermediate anneal. After swaging, the resulting wires were cut into 570 mm lengths and bent into the shape of a "U," each leg being approximately 260 mm long and the bottom section 50 mm. The wires were thoroughly degreased before being introduced into the ultrahigh vacuum doping chamber by etching them in a 1:1 solution of HF and HNO_3, rinsing with water and drying with acetone followed by methanol washes. For vanadium the procedure was the same except that the etch used was a 1:1 solution of HNO_3 and glacial acetic acid.

The U-shaped filament was inserted into the vacuum chamber and clamped to copper electrodes. The entire chamber was allowed to reach

TABLE 1

Manufacturer's Batch Analysis for VP Grade Tantalum (ppm/weight)

C	20.0	Co	< 10.0	Ni	< 10.0
H	9.0	Cr	< 30.0	Pb	< 10.0
O	65.0	Cu	< 10.0	Si	15.0
N	30.0	Fe	25.0	Sn	< 30.0
Ag	< 10.0	Mg	< 10.0	Ti	< 10.0
At	< 10.0	Mn	< 10.0	V	< 10.0
Bi	< 30.0	Mo	< 30.0	Zr	10.0
Ca	10.0	Nb	30.0		

TABLE 2

Manufacturer's Batch Analysis for VP Grade Vanadium (ppm/weight)

C	15.0	Cr	< 30.0	P	50.0
H	6.0	Cu	< 10.0	Pb	< 30.0
O	220.0	Fe	100.0	Sb	< 30.0
N	35.0	Mg	< 10.0	Si	500.0
Al	40.0	Mn	< 10.0	Sn	< 30.0
Bi	< 30.0	Mo	< 30.0	Ta	75.0
Ca	< 10.0	Nb	80.0	W	25.0
Co	< 10.0	Ni	10.0		

5×10^{-7} Torr, after which the metal was outgassed at 1273K by passing a 150 ampere AC current through the wire for fifteen to thirty minutes or until the pressure dropped again to 5×10^{-7} Torr. For doping, the top chamber was isolated from the pumping system by closing the interconnecting poppet valve. Doping of the wire was performed by admitting a partial pressure of the appropriate gas (ultra-high purity oxygen or nitrogen) through a precise leak valve. This pressure was maintained for one hour, the doping period. Once doping was finished, the heating current was switched off providing a relatively fast quench rate. The system was then reevacuated and the wire homogenized at 1273K under a dynamic vacuum of 5×10^{-7} Torr for fifteen to eighteen hours.

The procedure for the doping of tantalum with nitrogen was essentially the same except that the doping temperature was 1973K and the homogenizing time four days. The long time and high temperature produced a cross-section microstructure composed of one large central grain ($\sim$1.5 mm) surrounded by much smaller ($<40\mu$) grains. This structure reduces to basically single grains along the length of the sample once a gage section is machined.

After doping, the U-shaped filament was retrieved and microhardness tests were made on a cross-section cut from the short bend. The microhardness results were then compared with the data of Lohnert and Fromm (1) for determination of oxygen in tantalum; with that of Bradford and Carlson (2) for oxygen in vanadium; and that of Hörz (3) for nitrogen in tantalum. Almost 80 mm of metal near the electrodes must be discarded due to uneven heating. The rest of the filament, however, was available for machining into the miniature tensile specimens.

Tensile testing was performed on an Instron tensile testing machine Model C/D with a vertical tube furnace for high temperature testing. The tensile sample and high temperature grips were encased in a metal sheath which was flooded with flowing high purity argon which had been gettered by passing through heated titanium chips in an all metal system. The inert atmosphere was maintained during the high temperature tests and while cooling to ambient. Reduction in area determinations were done by using an average of four diameters from each sample, two orthogonal measurements performed on an x-y optical comparator from each half of the failed tensile samples.

B. Tantalum-Oxygen Results

Mechanical Properties

The major part of the research effort and hence the most extensive investigation was devoted to the tantalum-oxygen system. Figure 1 shows the reduction in area as a function of temperature for the concentrations 0.33, 0.85 and 1.35 atomic percent oxygen deformed at a strain-rate of $8.8 \times 10^{-4} sec^{-1}$. Limited data are also given for specimens with 0.50 atomic percent oxygen. These curves demonstrate that at this strain-rate all concentrations are capable of producing embrittlement between 550-900K and that the severity increases with increasing oxygen concentration. At room temperature there is very little effect on the ductility even at the highest oxygen concentration. Superimposed on this figure are the intervals of the three dynamic strain-aging effects and the high temperature region where surface cracking is seen to appear. A yield stress plateau is present from 300-600K; serrated yielding occurs from 450-600K; and an

increasing work hardening rate starts at room temperature increasing with temperature to a work hardening peak at 600K. The cross-hatching indicated on the high temperature half of Figure 1 indicates the temperature in which samples tested showed surface cracking along the gage section.

Figure 2 shows the loss in ductility as a function of strain-rate for the 0.33 atomic percent oxygen composition. Although the data are limited, the effect of strain-rate can be clearly seen. Decreasing the strain-rate from $8.8 \times 10^{-3} sec^{-1}$ to $8.8 \times 10^{-5} sec^{-1}$ lowers the reduction in area from over 95 percent to 55 percent. It is important to note that the same degree of embrittlement is seen in the niobium-oxygen system at equal strain-rates (4) but at almost two and a half times as much oxygen indicating that the embrittling effect of oxygen is much more severe in tantalum.

The parameter taken as a measure of the work hardening rate is the change in stress between the 0.2 percent offset yield point and that at 5 percent strain. The work hardening is very severe in this system reaching almost 450 MPa for the 1.30 atomic percent oxygen composition. The work hardening starts at room temperature for all compositions and increases to a maximum at approximately 600K. Comparison with the niobium-oxygen work hardening peak shows the tantalum-oxygen system to have much more active dynamic strain-aging taking place. A yield stress plateau is seen to start near room temperature and continue until about 600K. Serrated flow is seen to occur from 450-600K. Note that all three dynamic strain-aging effects accompany the ductility drop as shown in Figure 1.

Figure 3 is a schematic illustration of the basic load-elongation curves produced by samples tested at various temperatures in the embrittlement interval. Curve A represents the response of a ductile sample typical of Point A. This curve shows slight work hardening, maximum load and a fairly large necking strain. Curve B is typical of a sample tested at a slightly higher temperature and within the dynamic strain-aging interval. It shows an increased work hardening rate, maximum load and abrupt failure after a small necking strain. Curve C represents the behavior of a tensile sample showing full embrittlement, still within the dynamic strain-aging interval, and very close to the temperature of the work hardening peak. This curve shows the highest work hardening rate. Specimens failing around this point in the ductility minimum do so at maximum load or before as the load is still increasing. These failures show up as very sharp load drops in the recorder chart. Curve D is characteristic of samples failing in the high temperature side of the ductility minimum. These curves show an intermediate work hardening rate with failure showing up as a small necking strain followed by a gradual load drop. This behavior becomes most pronounced at slow strain-rates and, along with Figure 4, is evidence that at these temperatures failure is due to the slow propagation of a surface crack across the gage section. The high temperature failures with the gradual load drop shows the ability of the sample to partially support the applied load. These failures are in contrast to those seen at lower temperatures where the failure appears to be internally nucleated and propagates catastrophically once a critical stress is reached.

Fracture Studies

The fracture surfaces were studied in the scanning electron microscope and changes in the failure modes were noted. These studies showed a change in the characteristic fracture mode as the temperature was increased through the embrittlement interval. The low temperature (300-450K) fractures are characterized by surfaces showing microvoid coalescence typical of highly ductile failures. These specimens usually have above 70 percent reduction in area. Figure 5 corresponds to a specimen containing 1.30 atomic percent oxygen tested at 300K and is representative of the high ductility observed at low temperatures with all compositions. Within the brittle range (450-1000K) microvoids first become less deep and the cusps less pronounced as the temperature rises. This tendency continues to the point where eventually the rounded contours become angular and the fracture is largely intergranular in fully brittle specimens. There were no samples showing mixed ductile-brittle failure characteristics. In the alloy of 1.30 atomic percent oxygen this transition takes place very quickly as the ductility falls abruptly within a span of 50 degrees. Representative fractographs are shown in Figures 10 and 11 to show the high oxygen alloy at the start of embrittlement and in a fully brittle condition.

The brittle intergranular fractures within the ductility minimum have very little or no transgranular component. This is observed both in samples tested on the low temperature side of the ductility minimum where fracture is internally nucleated and in samples tested at higher temperatures where there is surface cracking and the failure is externally nucleated. This is in contrast to the fracture morphology observed in

the niobium-oxygen system where the basic fracture mode in the brittle region is transgranular quasi-cleavage with a secondary intergranular component. The nature of the fracture in the tantalum-oxygen specimens suggests either a segregation of oxygen to the grain boundaries or the precipitation of an oxide phase along the boundaries during crack propagation. No precipitates have been found either metallographically or at higher magnifications in the SEM.

The third type of fracture observed is characteristic of the high temperature return to ductility (1000-1300K). These fractures do not show the microvoids typical of low temperature ductility. Instead, there is a fibrous appearance to the fracture surface which at high magnification shows grain boundary sliding and shearing. The surfaces still show facets of grain boundaries, but these appear to have deformed and slipped over one another rather than separating with clean crisp facets.

Further Observations

The intergranular nature of the fracture suggested that perhaps a sensitization of the material might be occurring at elevated temperatures and causing precipitation of an intergranular oxide. In order to demonstrate that the embrittlement is characteristic of slow strain-rate embrittlement and that this condition does not persist after the material has cooled, a series of tests were performed on tantalum samples containing 0.7 atomic percent oxygen. Tensile samples were heated between 700 and 1273K for five minutes in the same tensile apparatus normally used for

testing. The samples were allowed to cool in a protective argon atmosphere and subsequently tested at room temperature. No embrittlement was found for specimens so tested; in fact the ductility was above 95 percent reduction in area in all cases. In order to ensure that this material was capable of undergoing slow strain-rate embrittlement, three tests were performed at 700K. These samples showed that ductility was reduced to 70 percent reduction in area. It is, therefore, concluded that the observed embrittlement is reversible, disappearing after the material is cooled to room temperature and is not a permanent condition.

The second part of these tests sought to establish at what point in the tensile test the observed surface cracks nucleated. The samples used for these tests contained 0.3 and 0.5 atomic percent oxygen and were tested in the manner previously described at $\dot{\varepsilon} = 8.8 \times 10^{-5} sec^{-1}$. The tensile tests were stopped after deforming to several different strains and the gage section was then examined in the SEM. The results of these experiments showed that cracking starts very early in the tensile test at strains as low as 1.5 percent and stresses less than one half of the ultimate stress. The cracks tended to nucleate at machining marks on the surface, and the crack propagation was not catastrophic. Figure 4 shows the surface cracks on the gage section and the partial propagation of one crack. If a high temperature test was stopped after allowing surface cracks to form and the tensile sample subsequently failed at room temperature, high ductility was observed. This is an interesting similarity to the cracking seen by Morlet, Johnson and Troiano (5) in hydrogen-charged steel strained 1.5 percent at room temperature. In their case, elimination of this effect was accomplished

by straining at liquid nitrogen temperatures. The elimination of cracking by straining at low temperature is similar to the elimination of cracks at the low temperature side of the ductility minimum of oxygen-charged tantalum and poses an intriguing link between hydrogen embrittlement and the more general slow strain-rate embrittlement.

C. The Vanadium-Oxygen Results

Results of the vanadium-oxygen system must be looked at with the consideration in mind that this metal as supplied contained a high level (7500 ppm) of titanium impurity. This impurity acted as a very active getter of oxygen when the oxygen concentration was high. Figure 9 shows the reduction in area as a function of temperature for three oxygen concentrations. The oxygen-free samples consisted of vanadium that was given the same heating sequence as the doped metal but without deliberate addition of oxygen. This metal showed no embrittlement as a function of temperature.

The second composition contained 0.2 atomic percent oxygen. Testing of these samples produced a ductility minimum centered at 700K. This minimum was preceded by a dynamic strain-aging interval in which (a) serrated yielding was seen from 520-650K; (b) a yield stress plateau occurred from 400-600K; and (c) an increasing work hardening rate was seen from room temperature to 600K. This pattern of dynamic strain-aging preceding the embrittlement in the vanadium-oxygen system was quite similar to that seen in the tantalum-oxygen and niobium-oxygen systems. Another similarity with these systems is the surface cracking

present at the high temperature side of the ductility minimum. In the low-oxygen vanadium alloy surface cracking was seen in specimens tested at 800 and 875K. Figure 11 shows the surface cracking present in the sample tested at 800K, which had ductility lowered to 72 percent reduction in area. The sample tested at 875K showed similar surface cracks but had minimal embrittlement, over 90 percent reduction in area. A sample tested at 1023K, also showing 90 percent reduction in area, did not have surface cracks indicating that there exists a temperature above which cracking disappears in oxygen-doped vanadium.

A third composition containing 0.8 atomic percent oxygen was then tested. This composition showed no ductility minimum. Instead, as can be seen in Figure 9, the alloy showed some overall embrittlement with reduced ductility over all temperatures tested but without evidencing a definite embrittlement interval. This composition produced no serrated flow and much-reduced yield stress plateau and work hardening rate. There was no evidence of surface cracking in specimens of this composition. Tests were performed at a strain-rate ten times slower than before to see if slowing down the test might bring out the embrittling effect. Figure 10 shows the reduction in area of the 0.8 atomic percent oxygen alloy tested at $\dot{\varepsilon} = 8.8 \times 10^{-4}$ and $8.8 \times 10^{-5} sec^{-1}$. It can be seen that reducing the strain-rate does not produce embrittlement in the 700K region as observed in the low oxygen alloy. Instead, the reduced ductility is seen from room temperature up to about 600K, precisely over the dynamic strain-aging interval. It is surmised that decreasing the strain-rate enhances the dynamic strain-aging effect even in the presence of high titanium concentration. This produces a pseudo-embrittlement due only to dynamic strain-aging.

The effect of small additions of titanium to vanadium was investigated metallographically. Figure 12 shows a dark band of precipitate which formed with a doughnut shape in the cross section of the wire. This dark band is presumed to be titanium oxides. It is believed that the ring formed inside the metal and not at the surface where all incoming oxygen would be expected to precipitate out because as oxygen diffused in it depleted the titanium in solid solution allowing oxygen to dissolve in the vanadium matrix of this zone. The metal used for these tests was examined under polarized light and found to contain a large number of grain boundary precipitates in the region where the dark ring appeared. Neither these precipitates nor the dark ring were observed in the low oxygen alloy (Figure 13).

D. Tantalum-Nitrogen Results

Homogenization of nitrogen in tantalum requires that the samples be heated to 1973K for four days. This produces essentially one very large grain across the gage section of a sample and perhaps only several grains along the length. In this system two compositions were made up. A high nitrogen composition containing 2.6 atomic percent nitrogen proved impossible to machine into tensile samples and was not tested. A second composition containing 0.3 atomic percent nitrogen proved workable and was tested with the following results.

Figure 14 shows the uniform elongation as a function of temperature for the 0.3 atomic percent nitrogen alloy. Uniform elongation rather than reduction in area is plotted because these samples failed in a chisel point. This is due to the very few grains making up the entire

specimen and producing failures typical of single grains. There is no loss in ductility as evidence by the uniform strain parameter. Figure 15 shows that nitrogen serves as a potent room temperature strengthener producing a room temperature yield stress almost twice that of oxygen-doped tantalum of similar composition. The yield stress drops sharply as soon as the temperature is raised. There is a small yield stress plateau between 500-600K indicating the presence of dynamic strain-aging effects. These effects are seen again in Figures 16 and 17, which show a work hardening peak at 600K. This peak coincides with the work hardening peak found in oxygen-doped tantalum but is much less pronounced. Inert fusion analysis of this metal by Gollob Analytical Services, Berkeley Heights, New Jersey, showed the oxygen content to be 112 ppm. These dynamic strain-aging effects are attributed to the oxygen, not nitrogen, content since strain-aging due to nitrogen is believed to occur at higher temperatures. Serrated yielding was observed between 620-780K which is almost 200 degrees above the temperature of serrated flow seen in oxygen-doped tantalum and is attributed to the effects of nitrogen. It is believed that this effect is occurring at a sufficiently high temperature for dynamic recovery to take place and obviate any further nitrogen effects. Since no embrittlement was seen, it is surmised that dynamic recovery is reducing the high stress levels to below that required for solute migration and possible embrittlement.

The fracture surfaces show some very interesting features characteristic of the near single crystal character of the cross-sections. In all cases failure was caused by the pulling down of the specimen into a chisel point. Slip bands showing a duplex slip system can be seen in

the lower temperature samples. As the temperature is increased, we see initially a more ductile fracture, then plastic flow lessens until superficial cracking is evident at 798K.

Discussion

That a slow strain-rate embrittlement similar to that caused by hydrogen in the transition metals could be produced by other interstitial elements was shown to exist by Donoso and Reed-Hill (6) in niobium-oxygen and was extensively studied by Watson (4). In this system, two ductility minima were discerned at low oxygen concentrations and fast strain-rates. Accompanying the lower temperature ductility minimum was an increasing work hardening rate. Both the onset of embrittlement and the work hardening peak shift to higher temperatures with increasing strain-rates. This work hardening increase occurs while the ductility is decreasing and precedes fully brittle behavior. The high temperature ductility minimum was characterized by the presence of a high degree of surface cracking which eventually disappeared as the temperature was raised beyond the limit of embrittlement. At the higher oxygen concentration or the slower strain-rates, the two distinct minima are not discernible having blended into one another. When this occurs, cracking is seen to start after the specimens show full embrittlement, almost half way into the ductility minimum.

There are strong similarities between the niobium-oxygen and tantalum-oxygen systems which imply that similar fracture mechanisms are at work. In this study it was shown that oxygen in tantalum produced one ductility

minimum which was composition and strain-rate dependent. The tantalum-oxygen system showed very active dynamic strain-aging occurring as demonstrated by the pronounced work hardening peak, yield stress plateau and presence of serrated flow. In this system also the low temperature side of the ductility drop was preceded by these effects and the specimen showed fully brittle behavior for a 200 degree temperature interval before any surface cracking was observed. All tantalum samples tested above 723K showed surface cracking. Even at the highest test temperature cracking was present.

Oxygen in tantalum produces a much more pronounced work hardening and embrittling effect than in niobium suggesting that this system may be an extreme case of what is seen in the niobium-oxygen system. In the tantalum-oxygen experiments testing was limited to temperatures below which there is a full return to ductility. It is hypothesized that cracking would disappear at a sufficiently high temperature.

The vanadium-oxygen system shows striking similarities with the tantalum-oxygen and niobium-oxygen systems. A small embrittling effect was found in a low-oxygen vanadium alloy. This embrittlement was also preceded by a strong work hardening peak, yield stress plateau and serrated flow. Also in this system, cracking was found in two samples tested at the high temperature limit of the ductility minimum. One of the samples with surface cracking showed marked embrittlement (800K) while the other showed a high degree of ductility (875K). A third sample examined showed no surface cracking at 1073K. Vanadium has the lowest melting point of these metals with a homologous temperature of

870K (0.4 Tm) and it is logical that the disappearance of cracking should be observed in this system. The lack of a ductility minimum in a higher oxygen alloy was due to the gettering action of the titanium impurity. It appeared that titanium was precipitating at the grain boundaries, thereby depleting the oxygen in solid solution. This conclusion is supported by polarized light microscopy of the two alloys where a grain boundary precipitate was observed in the high-oxygen alloy. Tests on this alloy showed that the dynamic strain-aging effects of the yield stress plateau and work hardening peak were highly attenuated and serrated yielding had been completely eliminated. The presence of precipitates acts as a strengthener producing higher yield and ultimate stresses with reduced ductility at all temperatures.

The tantalum-nitrogen system was the last system investigated. These experiments showed that no slow strain-rate embrittlement was produced by nitrogen in this metal. The slight work hardening is attributed to the 112 ppm oxygen impurity since this peak coincides with that of the oxygen-doped tantalum. This peak is very small in relation to that produced by the metal that was deliberately doped, but it shows that even a small concentration of oxygen is capable of increasing the work hardening rate. The serrations present in these tests are attributed to the nitrogen present in the metal since the temperature over which these are seen is much higher than those in the oxygen-doped metal. Cracking was present in the nitrogen alloys in specimens pulled at 798K and 973K, temperatures very close to those in which cracking appears in the oxygen alloys and is therefore attributed to the oxygen impurity.

The two oxygen-bearing metals have these features in common:

1. A ductility minimum which is composition and strain-rate dependent.
2. A low temperature side of the ductility minimum in which the loss in ductility is preceded by dynamic strain-aging effects; full embrittlement following the dynamic strain-aging work hardening peak.
3. The presence of surface cracking within the ductility minimum above some critical temperature.

In the low temperature side of the ductility minimum the fractures showed up as an abrupt drop in the Instron Chart indicating that the fracture travelled very quickly across the gage section. In the 1.33 atomic percent oxygen-tantalum alloy these failures occurred before the maximum load was reached. On the high temperature side of the ductility minimum, the fractures are externally nucleated at cracks along the gage section which form very early on in the tensile test. This cracking expands the gage section much like an accordion opening up until eventually one of the cracks becomes unstable and starts to propagate across the gage section. At these higher temperatures specimens with a high degree of embrittlement do not show a catastrophic load drop in the Instron Chart. Instead, a point of instability seems to appear and the load gradually drops as would occur if a crack were slowly propagating across the gage section. This effect becomes more pronounced at the slowest strain-rates when the cross-head speed is slow enough to permit the chart pen to record load variations as the crack opens up. The presence of cracking has been observed in the niobium-, vanadium-, and

tantalum-oxygen systems. This phenomenon is not isolated to metals containing oxygen impurity. Surface cracking was documented by Hardie and McIntyre (7) and Wood and Daniels (8) in hydrogen-charged niobium and by Morlet, Johnson and Troiano (9) in hydrogenated steel, so it appears that this behavior is common to metals containing other interstitials, not necessarily oxygen.

For equal concentrations of interstitial (0.3 atomic percent) the nitrogen in solution acts as a much more potent room temperature strengthener producing a yield stress that is almost twice that produced by oxygen. Increasing the temperature by 233 degrees drops the yield point by less than one third in the oxygen case while decreasing it almost twenty times in the nitrogen case. There is a very small work hardening effect in the nitrogen case which has been attributed to oxygen contamination, but overall the tendency is for the metal to lose strength with increasing temperature. This fact supports the conclusion that slow strain-rate embrittlement should not be caused by nitrogen because of onset of softening will not allow the large stresses necessary for the diffusion of the interstitial to develop.

The mechanism by which surface cracks nucleate is not completely clear. These cracks form early on in the tensile test and are seen to follow grain boundaries. There is evidence that slip processes in the surface grains of a polycrystalline sample are less restricted than in the interior grains and that the flow stress of the surface layers never becomes equal to the flow stress of the whole sample (10). If this is true, then there is a mechanism by which stress at quadruple points can be raised and become crack initiation sites. Nemy and Rhines (11) state

this process is caused by grains which are more favorably oriented for gliding (surface grains) moving away from those which are not (interior grains) thereby developing a hydrostatic tension at the quadruple point and nucleating a fissure. The fact that cracking is seen only above some critical temperature is consistent with Troiano's model since the temperature and strain-rate have to be such as to permit interstitial diffusion to the zone of hydrostatic tension. Once the fissure forms it can then move to the surface, become a surface crack and the conditions for slow strain-rate embrittlement are established.

The data presented show that the slow strain-rate embrittlement of metals generally attributed to hydrogen can be caused by at least one other interstitial, oxygen, in three transition metals. These results uphold the premise postulated by Troiano (12) twenty years ago that the slow strain-rate hydrogen embrittlement was a specific case of a more general phenomenon produced by the presence of mobile interstitial impurities in the transition metals.

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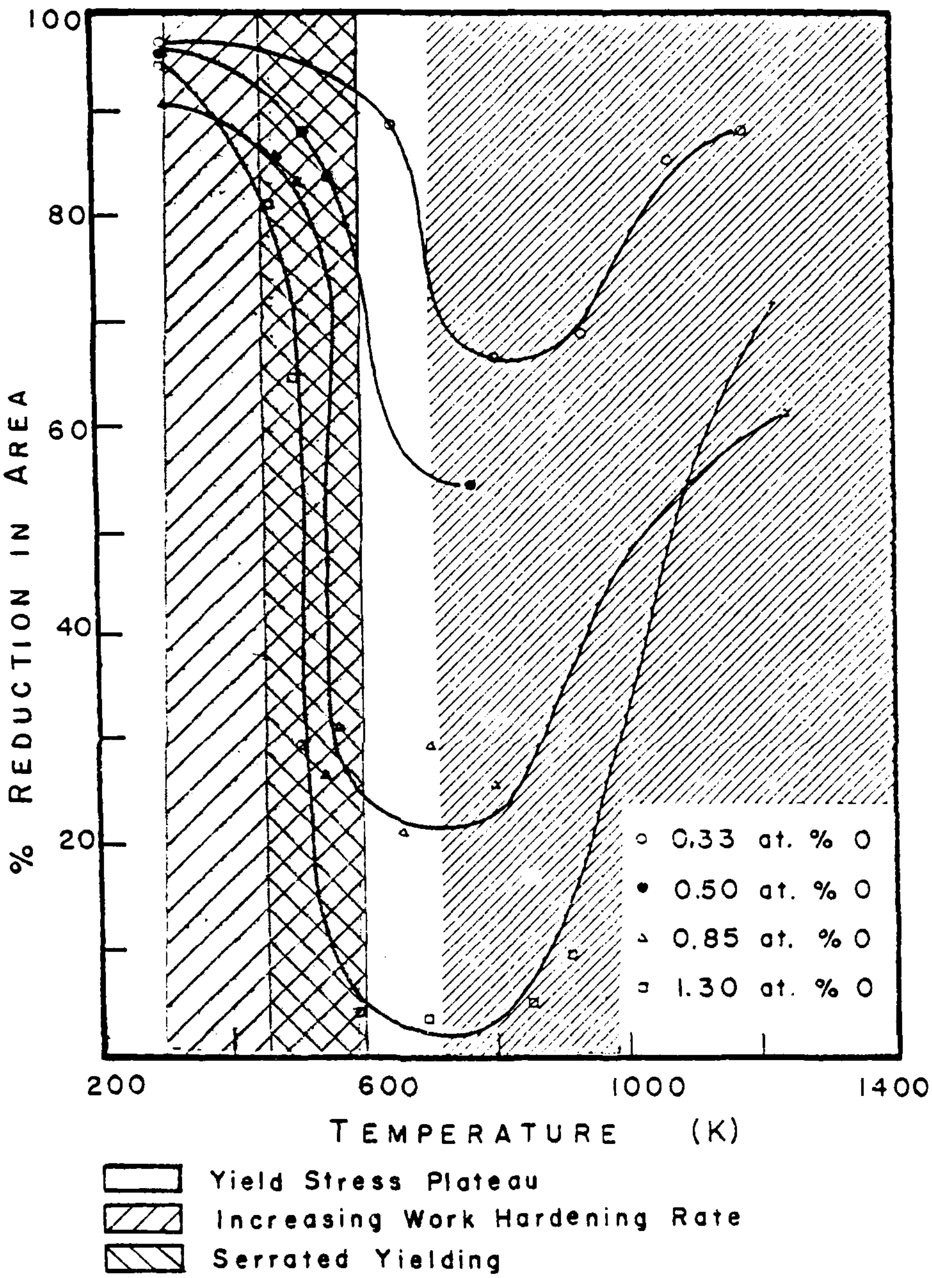


Figure 1. Reduction in area as a function of temperature for Ta-O showing dynamic strain-aging interval.

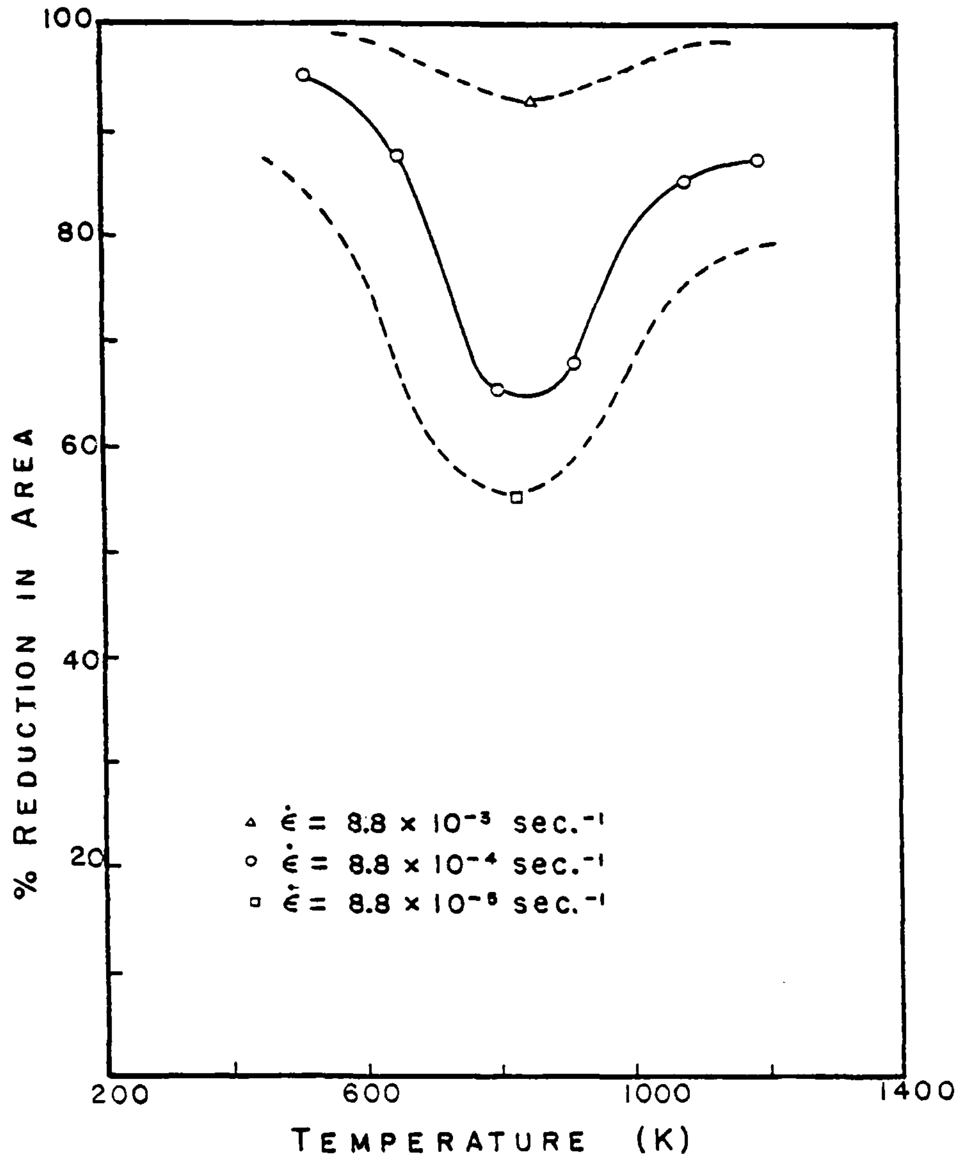
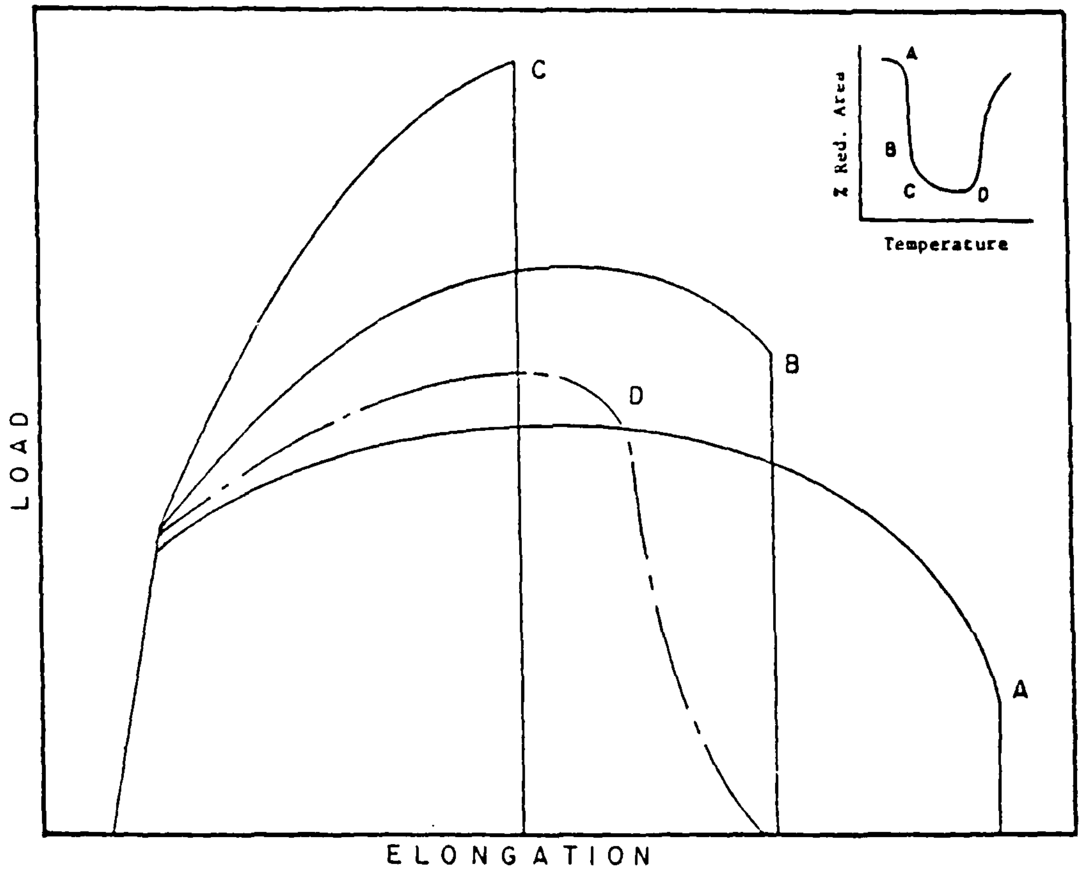


Figure 2. Reduction in area as a function of temperature for three strain-rates in the low O Ta-O alloy.



(A) Ductile fracture
(B) Partial embrittlement
(C) Low temperature embrittlement
(D) High temperature embrittlement

Figure 3. Schematic illustrations of the typical load-elongation charts at various points along the ductility minimum.

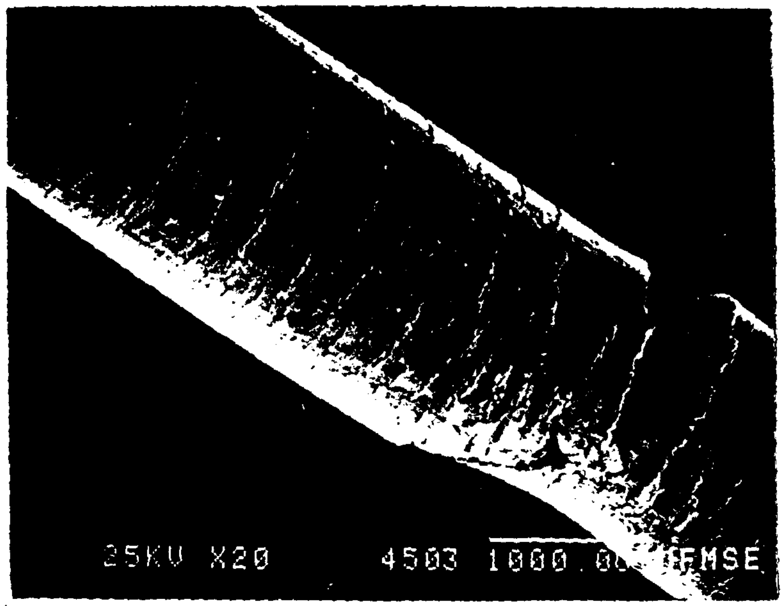


Figure 4. Scanning electron micrograph of a Ta specimen containing 0.5 atomic % O tested at 723K.

Figure 5. Room temperature fracture of the 1.30 atomic % O alloy showing high ductility.

Figure 6.

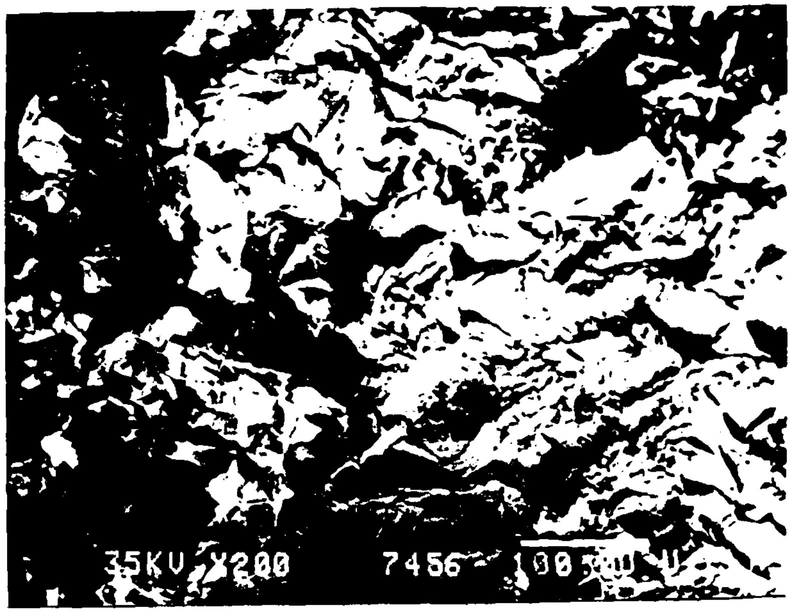


Figure 8.

Figure 7.

Figure 6. Fractograph of a 1.30 atomic % O alloy at 450K showing partial embrittlement.

Figure 7. Fractograph of a 1.30 atomic % O alloy at 690K showing the intergranular fracture mode of brittle specimens.

Figure 8. Fractograph of a 1.30 atomic % O alloy tested at 1013K showing high temperature ductility.

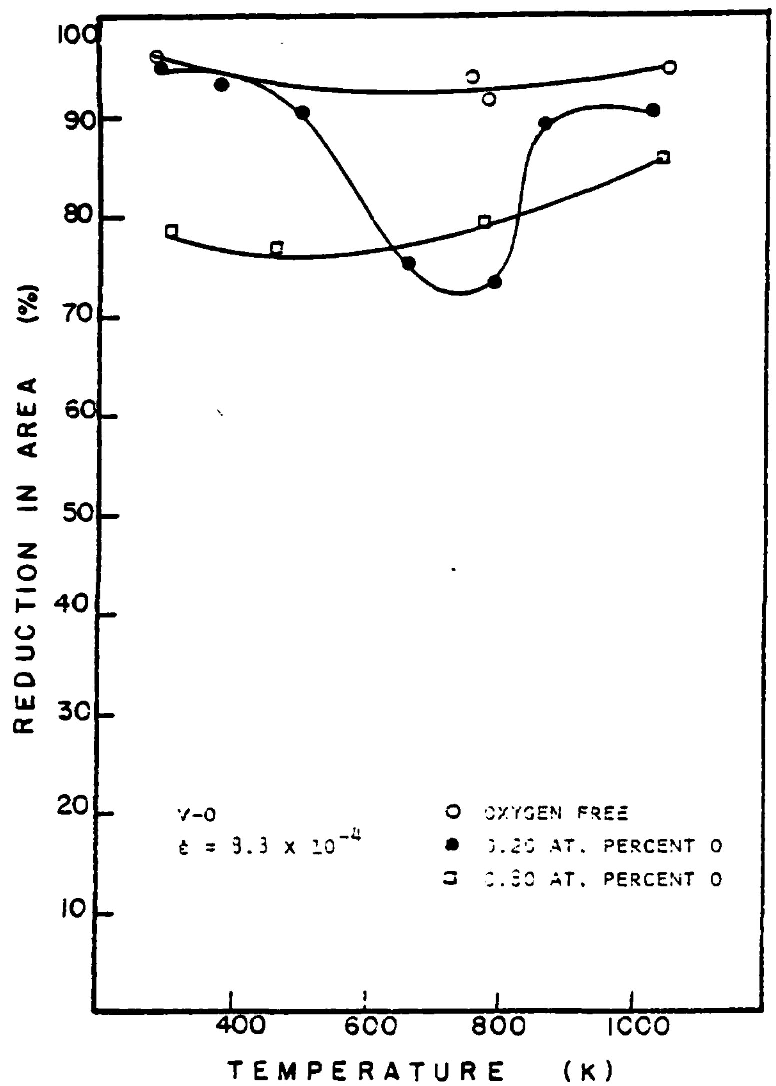


Figure 9. Reduction in area as a function of temperature for three compositions. Serrated flow was present from 520 to 650K.

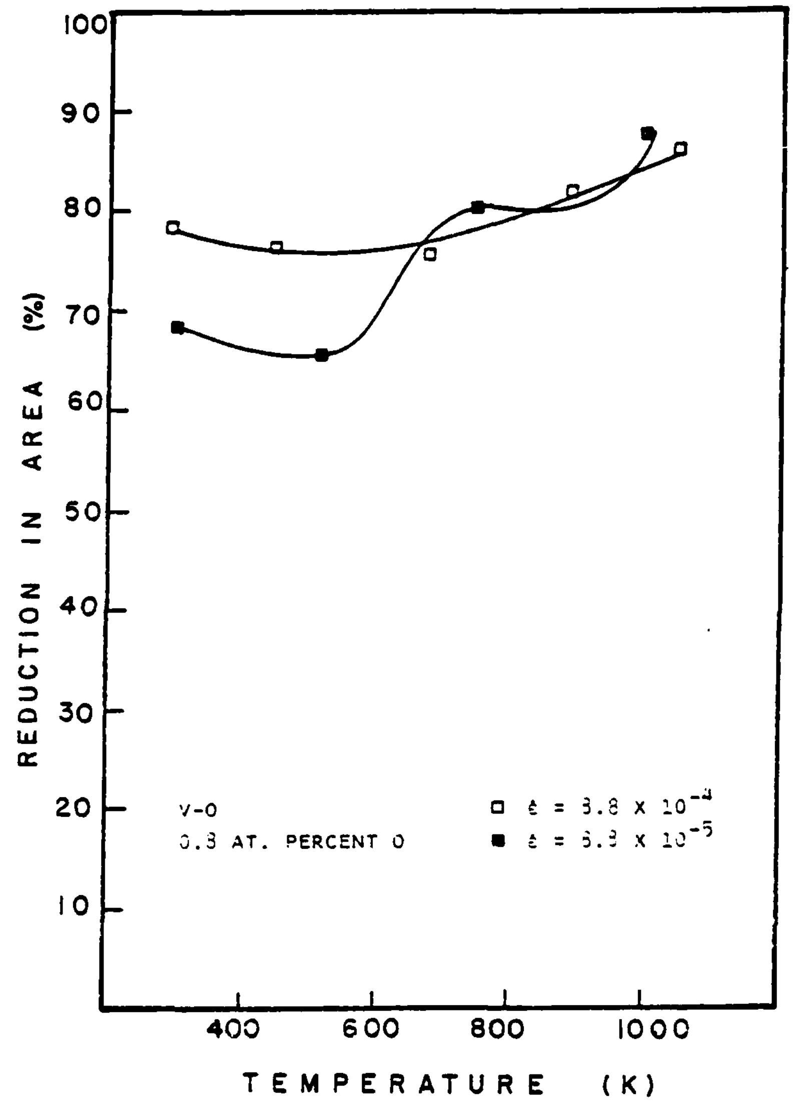


Figure 10. Reduction in area as a function of temperature for 0.8 atomic % O in vanadium at two strain-rates.

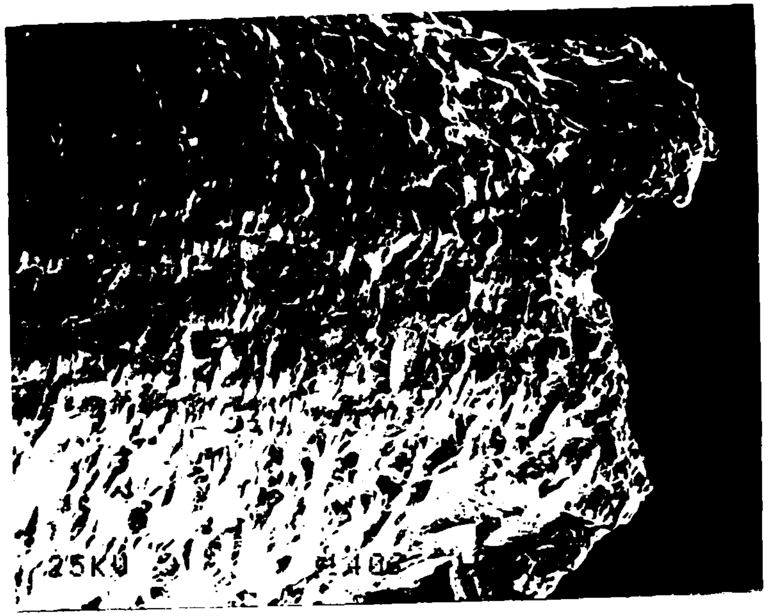


Figure 11.

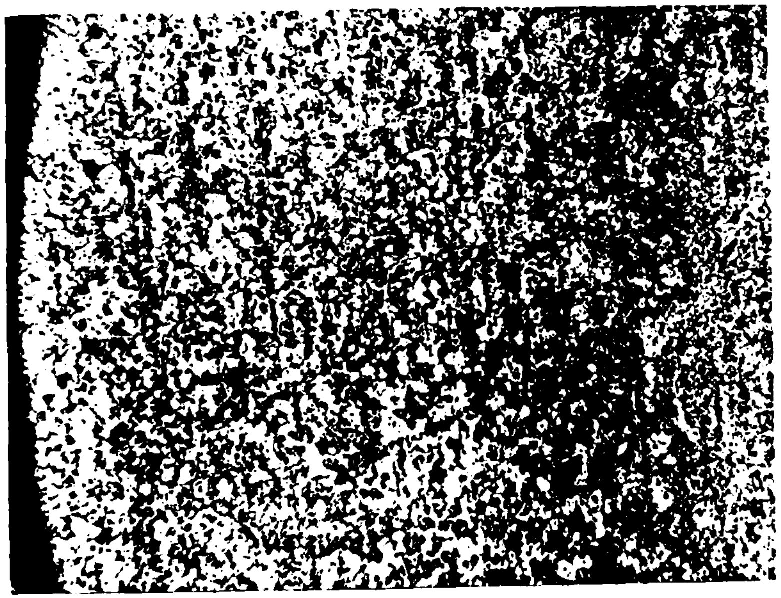


Figure 12.

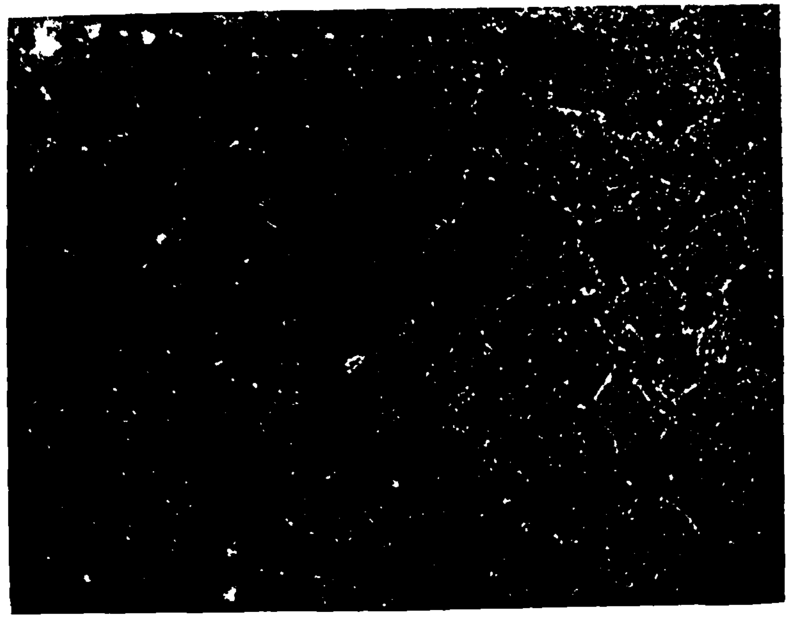


Figure 13.

Figure 11. Scanning electron micrograph of a 0.2 atomic % O vanadium sample tested at 800 K.

Figure 12. Micrograph of precipitate band in 0.8 atomic % O in vanadium with 7500 ppm titanium impurity.

Figure 13. Polarized light micrograph of grain boundary precipitates in 0.8 atomic % O in vanadium with 7500 ppm titanium impurity.

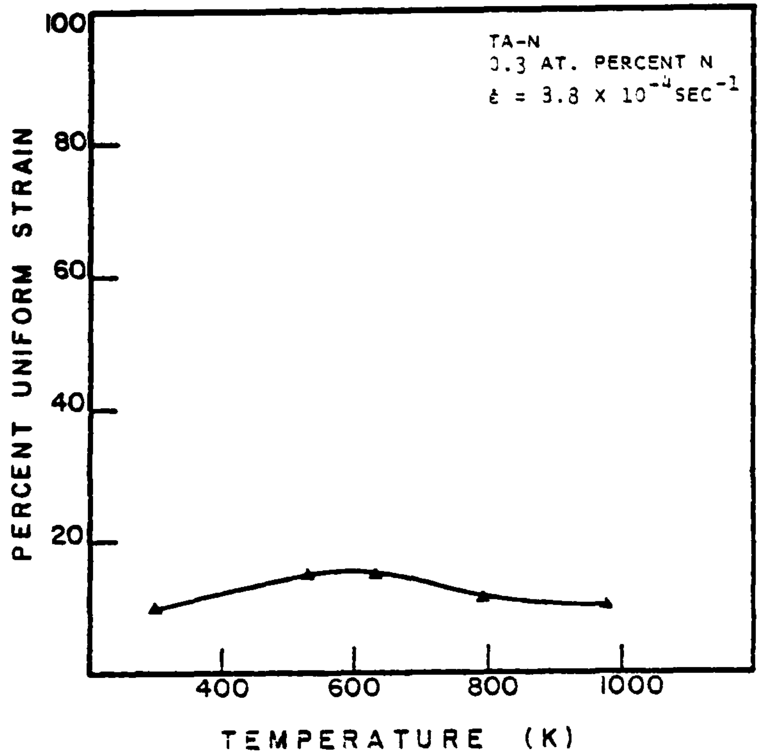


Figure 14. Plot of the uniform strain as a function of temperature for a Ta 0.3 atomic % N alloy.

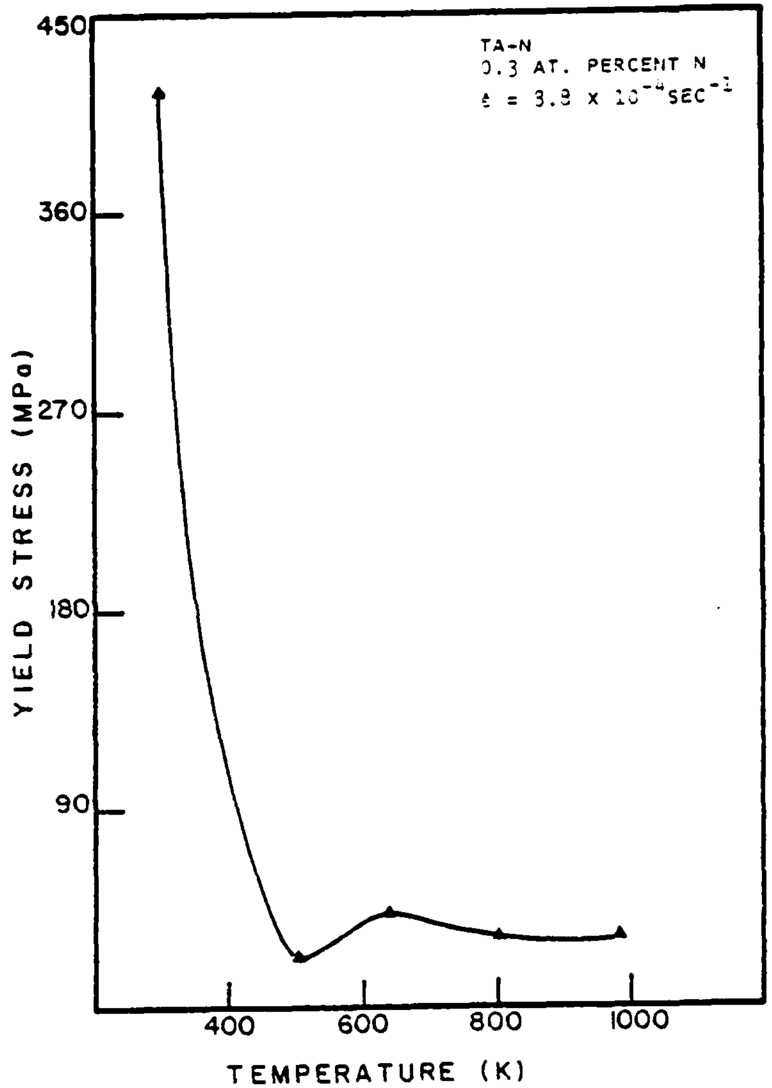


Figure 15. Plot of the yield stress as a function of temperature for a Ta 0.3 atomic % N alloy.

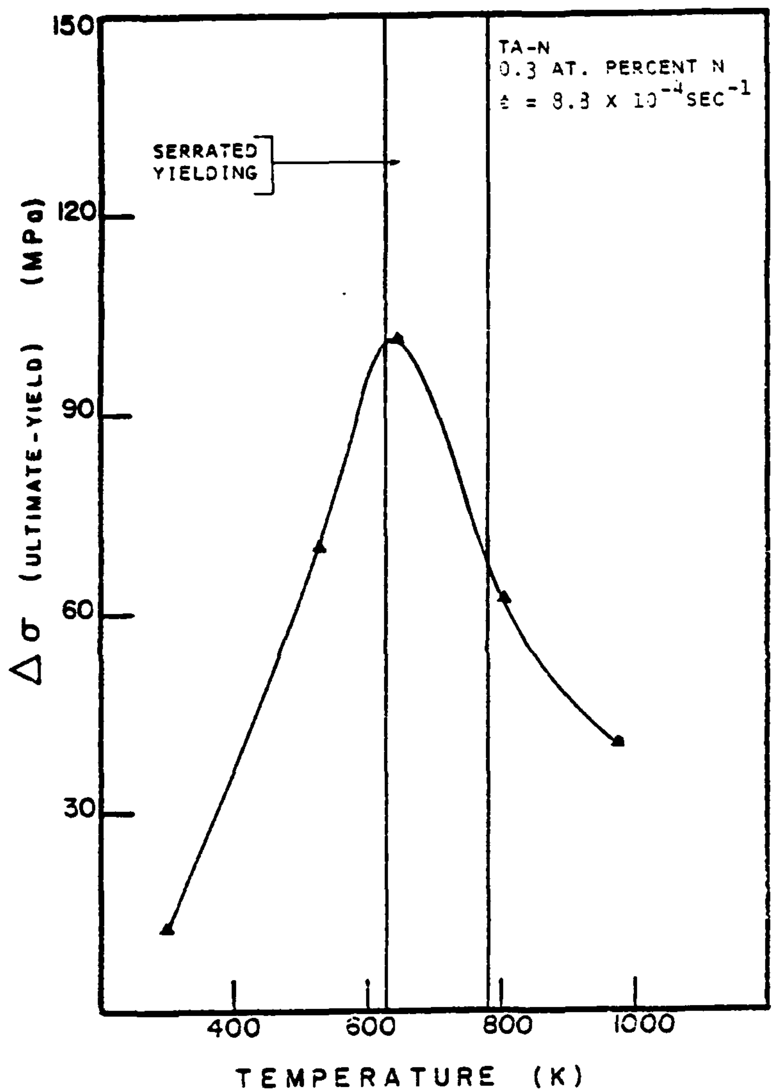


Figure 16. Plot of the work hardening rate in a Ta 0.3 atomic % N alloy.

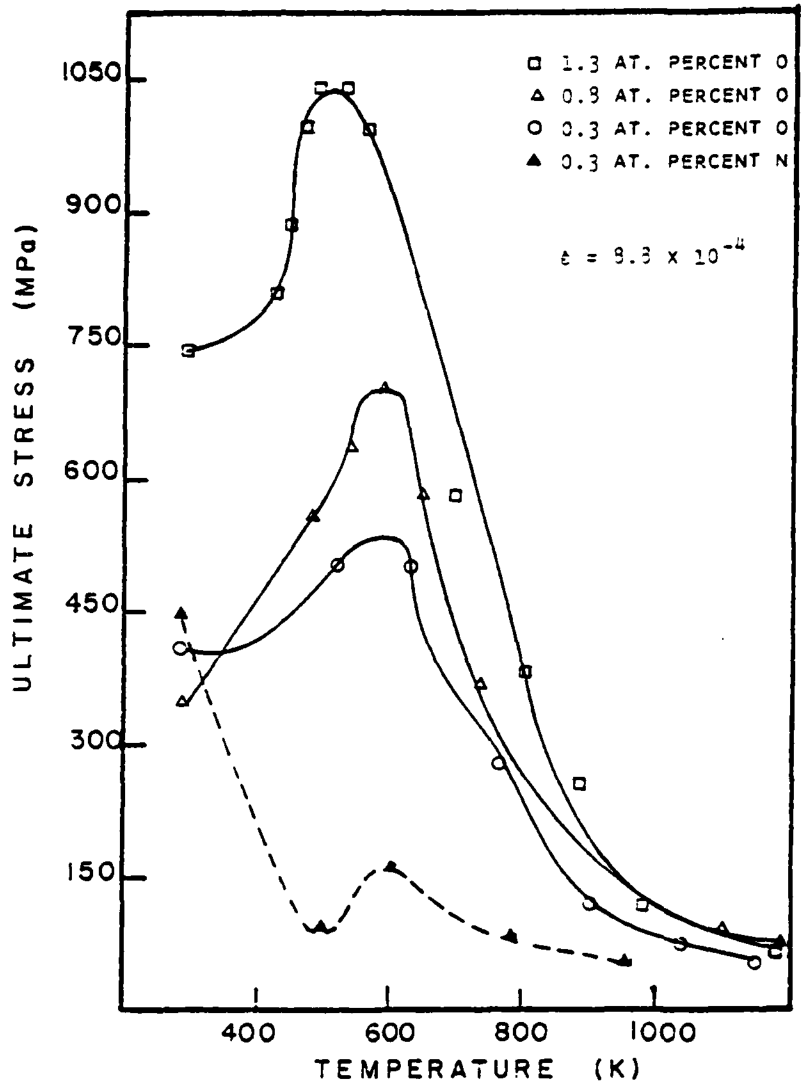


Figure 17. Plot of the ultimate stress as a function of temperature for three levels of oxygen and one of nitrogen in Ta.

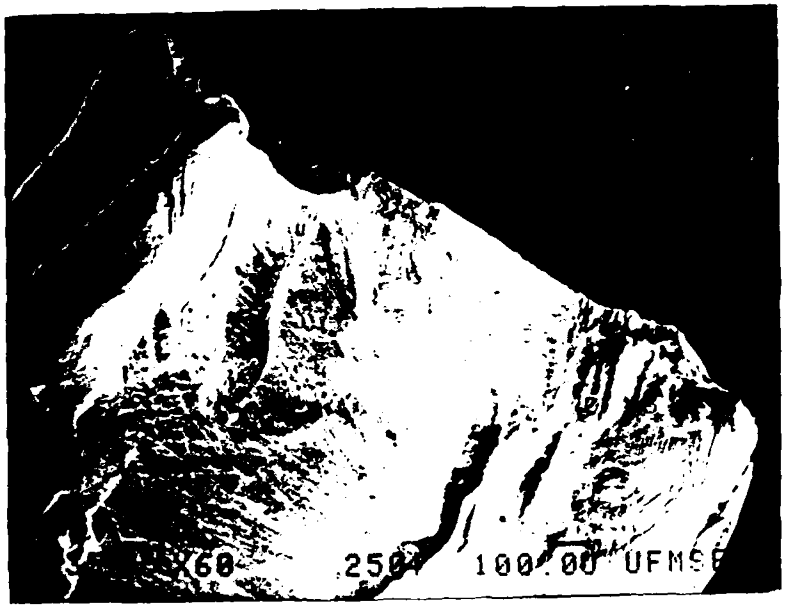


Figure 18.

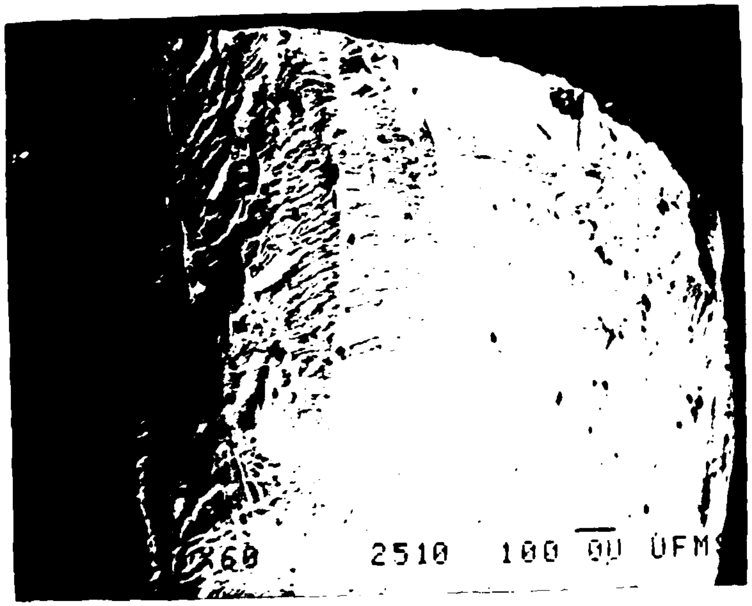


Figure 19.

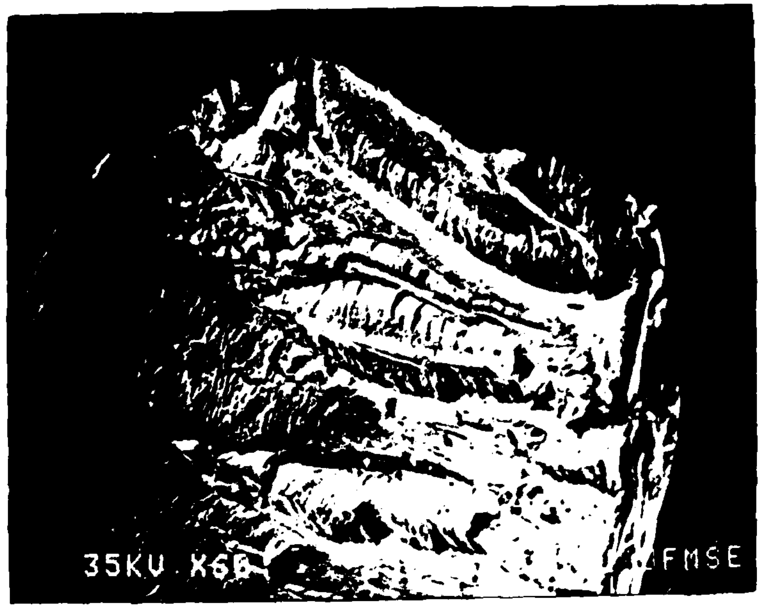


Figure 20.

Figure 18. Scanning electron micrograph of the fracture surface of a Ta 0.3 atomic % N alloy tested at 300K.

Figure 19. Scanning electron micrograph of the fracture surface of a Ta 0.3 atomic % N alloy tested at 636K.

Figure 20. Scanning electron micrograph of the fracture surface of a Ta 0.3 atomic % N alloy tested at 973K.